FINAL REPORT – DOE LABORATORY PARTNERSHIP AWARD

Report Period : 6/1/2003 – 5/31/2007

Fundamental Mechanistic Investigations of Silane and Chlorocarbon Addition to Low Valent Palladium Species and their Application to Catalysis

(6/1/2003 – 5/31/2007)

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Discussion of Status

This final report covers the period from June 15, 2003 to July 15, 2007. During this project period, new equipment was purchased and installed, a postdoctoral associate was hired, a graduate student and an undergraduate student were recruited for the project, as well as several visits between us and our DOE partners. A number of important scientific milestones were met which are discussed later in the report.

Collaboration with DOE Partner: The project is an active collaboration with Morris Bullock and Etsuko Fujita at Brookhaven National Laboratory (BNL). I met with Etsuko Fujita, who manages the transient IR facility at BNL, during July 2004. We discussed specific projects to be conducted at BNL as part of the collaboration. Subsequently, Morris Bullock visited Tulane in September of 2004 to discuss the collaboration. In the Fall of 2005, Douglas Pool (a postdoctoral assistant) and Daniel Sattler (a graduate student) spent several months at BNL due to the impact of Hurricane Katrina. The displaced personnel benefitted greatly in an uninterrupted work flow and the ability to directly interact with Dr. Morris Bullock (now at PNL) and Dr. Etsuko Fujita at BNL.

Progress Against Schedule/Milestones stated in DOE EPSCoR Proposal

Excellent progress has been made since the last annual report. All of the major milestones stated in previous year's annual report have essentially been met.

Significant Findings/Events/Accomplishments

Background

There has been great recent interest in dicoordinate palladium (0) complexes bearing chelating bisphosphine ligands, (P^P)Pd. These extremely reactive complexes are capable of activating aromatic C-Cl bonds and have been proposed as key intermediates involved in the rate-limiting steps of a number of particularly important synthetic reactions including catalytic aromatic dehaloamination[1] and Heck type reactions.[2] The very high reactivity of these (P-P)Pd complexes is attributable to the nonlinear coordination environment about the palladium, enforced by the chelating bisphosphine. Using Extended Huckel calculations, Hofmann has shown that the frontier orbitals of $(H_3P)_2Pt$ dramatically change as a function

of P-Pt-P bond angle.[3] The result of increased bending results in smaller HOMO-LUMO gaps and spawns an isolobal analogy to singlet carbenes. The very high "carbenic" reactivity of these complexes is reflected in the ability of these complexes to undergo facile C-H additions as demonstrated by Hofmann[3] and Whitesides.[4]

A similar analogy exists for the palladium analogs. We have performed Extend Huckel calaculations on $(H_3P)_2Pd$ and found the results to be qualitatively in accord with Hofmann's work on the platinum systems. In our laboratory, we have been able to generate (P^P)Pd intermediates from either the photolysis of oxalates,[5] reduction of Pd(II) acetates and halides,[6] or reductive elimination of ethane from dimethyl palladium complexes (P^P = chelating diphosphine).[7] Due to their high reactivity, none of the low coordinate (P^P)Pd complexes are stable at room temperature. Evidence for the generation of (P^P)Pd intermediates comes from the formation of unusual d^{10}-d^{10} palladium dimers. In contrast to the platinum analogs, the "carbenic" palladium species has no tendency to undergo C-H insertion reactions. In respect to catalysis, this makes this intermediate *less reactive and more selective* than the platinum analogs. Most importantly, the lack of reactivity with C-H bonds allows these potentially catalytic intermediates to be compatible with most organic solvents.

In catalytic systems, (P^P)Pd is often generated by ligand dissociation form $(P^P)PdL_n$ where L is often another phosphine or dibenzylideneacetone (dba).[8] This gives very low equilibrium concentrations of (P^P)Pd which usually prevents direct detection and makes mechanistic interpretations challenging. However, some progress has been made in this area. For instance, Milstein has investigated the reaction of $(dippe)_2Pd$ [dippe = 1,2-bis(diisopropyl-phosphino)propane] with a series of chloroarenes and was able to characterize the transition state for C-Cl insertion by (P^P)Pd using Hammett relationships.[9] Although direct rate constant data was ultimately extracted, the task was complex due to the presence of competing ligand redistribution reactions in this system.

Direct rate constant data should be more straightforwardly obtained through laser flash photolysis studies in which a (P^P)Pd intermediate is generated in the absence of extraneous ligands. A number of photochemical precursors to zero-valent Pd complexes have been reported in the literature. Most notable is the photolysis of (dcpe)Pd(oxalate) which we discovered to give quantitatively the dimer of the zero valent intermediate (dcpe)Pd, [dcpe = 1,2bis(dicyclophosphino)ethane].[5] Other reasonable photochemical sources include bis(azido)

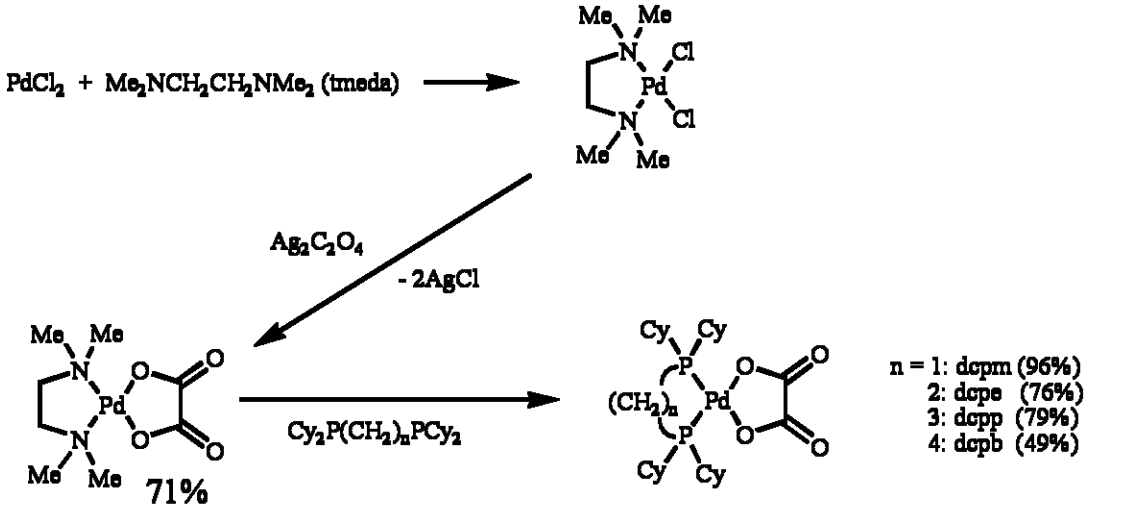
and dialkyl palladium species.

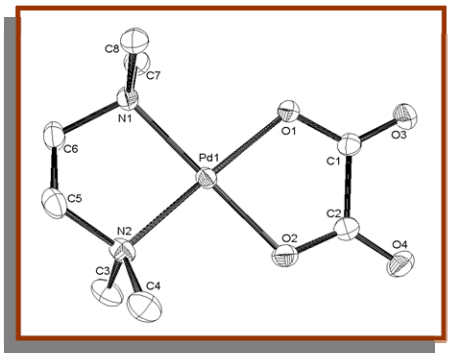
One goal of the project was to examine the potential intereaction of the (P^P)Pd reactive intermediates with the Si-H bond. Although palladium complexes are established hydrosilylation catalysts, very little is known about compounds containing a palladium-silicon bond. Very recently, we have been able to directly observe the first examples of silyl palladium hydrides from the reaction of $[(dcpe)Pd]_2$ with tertiary silanes.[10] In general, the complexes are unstable to the slow reductive elimination of silane and therefore must be characterized in the presence of excess silane. The stability of these complexes is enhanced by the degree of phenyl substitution on silicon, and in the case of $(dcpe)Pd(SiPh_3)H$, we were able to isolate the complex and determine its structure by X-ray crystallography. The solid state structure of $(dcpe)Pd(SiPh_3)H$ reveals a square planar coordination environment at the palladium typical of a Pd(II) complex.

The NMR behavior of $(dcpe)Pd(SiPh_3)H$, as well as other observed silyl palladium hydrides, reveal a high degree of fluxionality in these complexes due to the rapid interchange of silyl and hydride environments This high degree of fluxionality is likely mediated by an intermediate $^2\eta$-Si-H complex. Activation parameters, obtained from variable temperature ^{31}P and ^1H NMR measurements of $(dcpe)Pd(SiR_3)H$ and $(dcpe)Pd(SiR_3)D$ complexes, revealed a hydride KIE which at lower temperatures is strongly inverse (.25-.35) but becomes strongly normal at higher temperatures (5-7).[10] Although all aspects of this unusual isotope behavior have not been elucidated, two points are clear: 1) the rearrangement is likely a multi-step process with a change in rate limiting step over the observed temperature range, and 2) quantum mechanical tunneling is a strong contributor due to the large magnitude of the effect. The implication of a multi-step mechanism provides strong indirect support for a $^2\eta$ -Si-H intermediate. The low barriers to activation imply that the $^2\eta$ -Si-H intermediate is very close in energy to the silyl palladium hydride and may be mechanistically important in the reaction chemistry of silyl palladium hydrides. The implication of $^2\eta$ -Si-H intermediate in a fluxional process is also important in respect to silicon-hydrogen bond activation since it is a likely intermediate on this pathway as well.

Photochemical Precursors to Low Valent Palladium:

A significant goal of this project is the photochemical generation of highly reactive low coordinate palladium intermediates of the type (P^P)Pd where (P^P) is a chelating bisphosphine. The size of the P^P chelate ring is expected to dramatically modulate the reactivity of the Pd center of the reactive intermediate (P^P)Pd. One potential class of photochemical precursors are the corresponding palladium oxalates, (P^P)Pd(C_2O_4). A new general route to bisphosphine palladium oxalates was developed in our laboratories. The reaction involves the synthesis of the new complex, (tmeda)Pd(oxalate), as a key intermediate species. The tmeda ligand of the complex is easily displaced by bisphosphines to give the corresponding bisphosphine oxalates (Figure 1). An X-ray crystal structure of the (tmeda)Pd(oxalate) complex has been obtained.





Complex	Main Oxalate Stretching Frequency
dcpmPdC$_2$O$_4$	1656 cm^{-1}
dcpePdC$_2$O$_4$	1662 cm^{-1}
dcppPdC$_2$O$_4$	1668 cm^{-1}
dcpbPdC$_2$O$_4$	1673 cm^{-1}

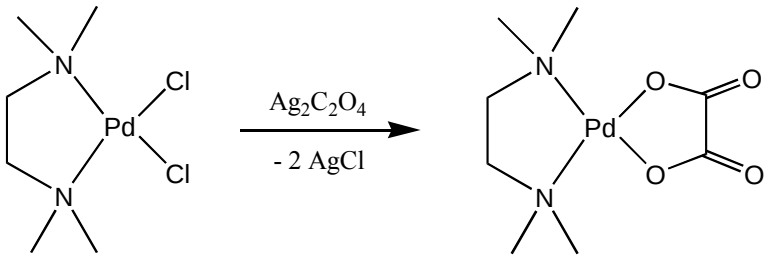
Figure 1. General Synthesis of Palladium Oxalates with X-Ray Structure of (tmeda)PdC$_2$O$_4$

Synthesis of Palladium Oxalates

Synthesis of (tmeda)$PdCl_2$

The complex (tmeda)$PdCl_2$ reacts with an excess of silver oxalate in refluxing methylene chloride to produce (tmeda)PdC_2O_4 (Scheme 1). The product precipitates leaving a saturated yellow solution. Soxhlet extraction of the resulting solid with CH_2Cl_2 allows for product separation from the AgCl generated in the reaction. Yellow crystals of (tmeda)PdC_2O_4 grow from CH_2Cl_2 and pentane at –20° C. The combined isolated yield from the initial filtrate and the extraction of the solid mixture is 71%.

The ^{1}H NMR spectrum contains two singlets consistent with the tmeda ligand at 2.78 and 2.64 ppm. Integration is consistent with four CH_2 protons and 12 methyl protons respectively. The $^{13}C\{^1H\}$ NMR spectrum contains three peaks at 165.8, 60.8, and 49.7 ppm. These peaks are consistent for the oxalate group and the methylene and methyl groups of the tmeda ligand. The IR spectrum contains three intense stretching frequencies at 1703, 1678, and 1660 cm^{-1} corresponding to C=O vibrations of the oxalate ligand.



Scheme 1

The crystal structure for (tmeda)PdC_2O_4 shows two independent molecules of oxalate complex as well as two independent CH_2Cl_2 molecules in the asymmetric unit. One of the oxalate molecules suffers disorder in the tmeda ligand. The geometry around the Pd centers is distorted square planar as seen in Figure 1. The bond distances for the two independent molecules in the asymmetric unit are within experimental error of each other (Table 1). The average Pd-O bond distance is 2.012 Å and the average Pd-N bond

distance is 2.032 Å. The O-Pd-O and N-Pd-N angles for the two bidentate ligands are constrained to less than 90° causing the N-Pd-O bond angles to be greater than 90°.

Table 1. Bond distances and bond angles for tmedaPdC_2O_4.

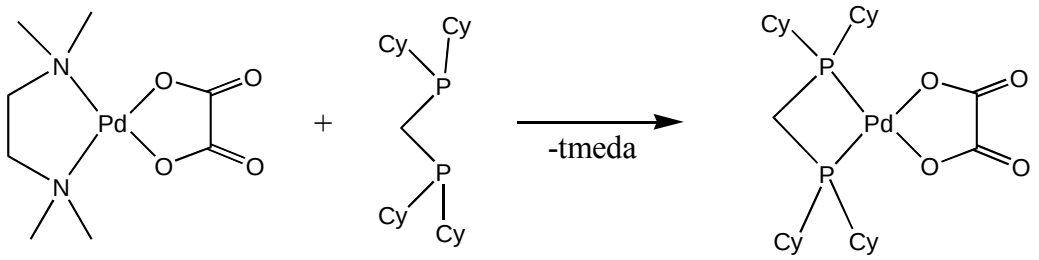
Atoms	Bond Distance (Å)	Atoms	Bond Angle (degrees)
Pd1-O1	2.013(2)	O1-Pd1-O2	83.62(10)
Pd1-O2	2.011(3)	N2-Pd1-O2	94.65(11)
Pd1-N1	2.033(3)	O1-Pd1-N2	177.32(11)
Pd1-N2	2.032(3)	O2-Pd1-N1	178.19(11)
Pd2-O5	2.011(3)	O1-Pd1-N1	95.32(11)
Pd2-O6	2.011(2)	N2-Pd1-N1	86.47(12)
Pd2-N3	2.029(3)	O5-Pd2-O6	83.58(10)
Pd2-N4	2.033(3)	O5-Pd2-N3	95.13(12)
		O6-Pd2-N3	178.53(12)
		O5-Pd2-N4	178.36(12)
		O6-Pd2-N4	95.06(11)
		N3-Pd2-N4	86.25(13)

The complex (tmeda)PdC_2O_4 reacts with diphosphines which readily replace the tmeda ligand. An excess of phosphine is necessary to drive the reaction to completion in a reasonably short time. The lengthy dissolution of the phosphine palladium oxalate complexes in CH_2Cl_2 results in the formation of the corresponding phosphine palladium dichloride. Quick isolation of the product at low temperatures slows or prevents this unwanted reaction.

Synthesis of (dcpm)PdC_2O_4

The reaction of (tmeda)PdC_2O_4 and bis(dicyclohexylphosphino)methane (dcpm) (Scheme 2) in CH_2Cl_2 under nitrogen for 13 hr gave a white precipitate in a colorless solution. The amount of solid increased with the addition of pentane and cooling the mixture. The yield of the white solid was 96%. Though the (dcpm)PdC_2O_4 is not very

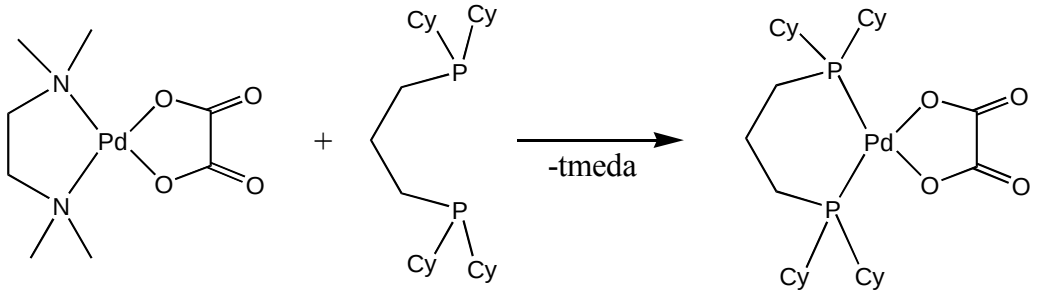
soluble in CD_2Cl_2, enough dissolved to characterize it by NMR. The ^1H NMR spectrum contains multiplets for the Cy groups between 1.2 ppm and 2.2 ppm and a triplet for the methylene backbone of the phosphine at 2.83 ppm consistent with identical protons coupled to two identical phosphorus atoms. The $^{31}P\{^1H\}$ NMR spectrum has one singlet at –27.3 ppm. The IR spectrum contains a single sharp stretching frequency at 1662 cm^{-1} with a shoulder peak at 1637 cm^{-1} and a smaller peak at 1702 cm^{-1} corresponding to the oxalate group.



Scheme 2

Synthesis of (dcpp)PdC_2O_4

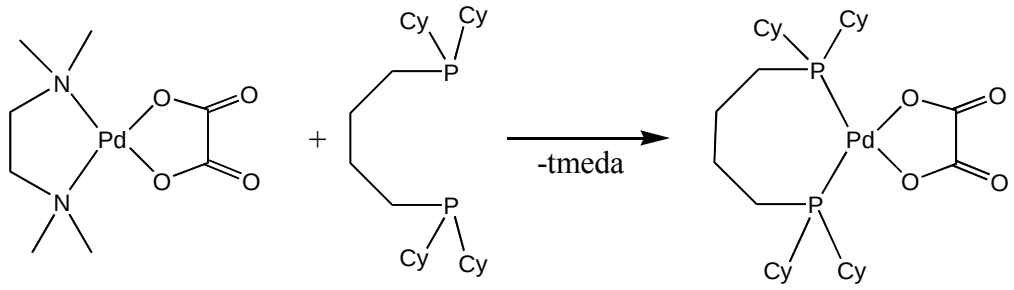
The combination of (tmeda)PdC_2O_4 and bis(dicyclohexylphosphino)propane (dcpp) (Scheme 3) in CH_2Cl_2 under nitrogen with stirring for 1 hr gave clear colorless solution. The addition of pentane and the cooling of the solution gave (dcpp)PdC_2O_4 as a white solid. The combined yield from a first and second crop was 74%. The ^1H NMR spectrum contains multiplets between 1.2 ppm and 2.3 ppm consistent for Cy groups. The $^{31}P\{^1H\}$ NMR spectrum has one singlet at 31.5 ppm. The IR spectrum contains a strong signal at 1668 cm^{-1} with smaller peaks at 1697 and 1647 cm^{-1} corresponding to the oxalate group.



Scheme 3

Synthesis of (dcpb)PdC_2O_4

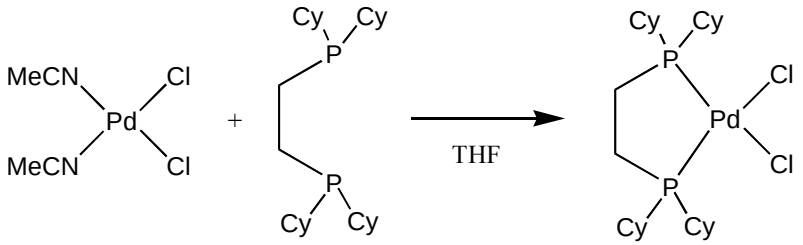
The combination of (tmeda)PdC_2O_4 and bis(dicyclohexylphosphino)butane (dcpb) (Scheme 4) in CH_2Cl_2 under nitrogen with stirring for 12 hr gave clear colorless solution with yellow solid that was easily removed by filtration. The addition of pentane to the solution and maintaining it at –20°C yielded dcpbPdC_2O_4 as a white powder. The ^1H NMR spectrum contains multiplets between 1.2 ppm and 2.3 ppm consistent for Cy groups. The $^{31}P\{^1H\}$ NMR spectrum had a single peak at 44.3 ppm. Obtaining another $^{31}P\{^1H\}$ NMR spectrum three days later using the same NMR sample in CD_2Cl_2 showed the presence of an additional peak at 46.2 ppm corresponding to (dcpb)$PdCl_2$. The IR spectrum for (dcpb)PdC_2O_4 has one main stretching frequency at 1673 cm^{-1} and smaller peaks at 1697 and 1647 cm^{-1}.



Scheme 4

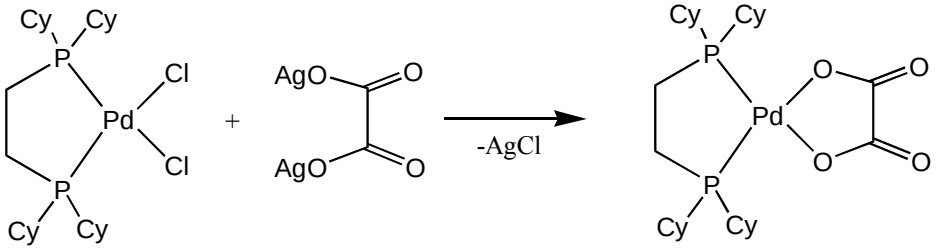
Synthesis of (dcpe)PdC_2O_4

The complex $(MeCN)_2PdCl_2$ reacts with bis(dicyclohexylphosphino)ethane (dcpe) in THF when stirred for 12 hours under nitrogen to form (dcpe)$PdCl_2$ (Scheme 5) in near quantitative yield. The $(MeCN)_2PdCl_2$ gradually goes into solution to react and form a white precipitate. The $^{31}P\{^1H\}$NMR has one singlet at 94.6 ppm characteristic for this compound.



Scheme 5

The complex (dcpe)$PdCl_2$ reacts with an excess of $Ag_2C_2O_4$ in refluxing CH_2Cl_2 or MeOH to give (dcpe)PdC_2O_4 (Scheme 6). Recrystallization of (dcpe)PdC_2O_4 from distilled CH_2Cl_2 and pentane at –20° C gave white solid. The $^{31}P\{^1H\}$NMR has one singlet at 89.8 ppm characteristic for this compound. The UV-visible spectrum contains a λ_{max} at 212 nm in MeCN. The IR spectrum has a strong stretching frequency at 1662 cm^{-1} and two shorter peaks at 1698 and 1639 cm^{-1}.



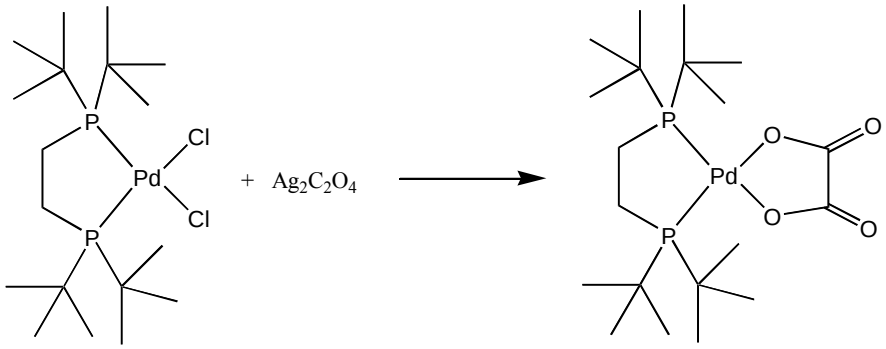
Scheme 6

Synthesis of (dtbpe)PdC_2O_4

The phosphine dtbpe (bis(di-*t*-butylphosphino)ethane) reacts with $(MeCN)_2PdCl_2$ in THF to form (dtbpe)$PdCl_2$ (Scheme 7) and orange insoluble material. The slow addition of the phosphine to a stirred THF suspension of $(MeCN)_2PdCl_2$ decreased the amount of insoluble material generated in the reaction. Treatment of $CODPdCl_2$ with dtbpe gave a homogeneous yellow solution that contains mostly (dtbpe)$PdCl_2$ when analyzed by NMR. Crystallization from CH_2Cl_2 and pentane gave light yellow needle crystals.

The ^1H NMR spectrum for (dtbpe)$PdCl_2$ contains two doublets with second order influence at 1.54 and 2.02 ppm. The ratio of the integrated area for these two signals is 36:4, the expected value for the (dtbpe)$PdCl_2$ ligand. The $^{31}P\{^1H\}$ NMR contains one

singlet at 103.4 ppm. The reaction of the (dtbpe)$PdCl_2$ complex with AgC_2O_4 in methylene chloride yield the corresponding oxalate.



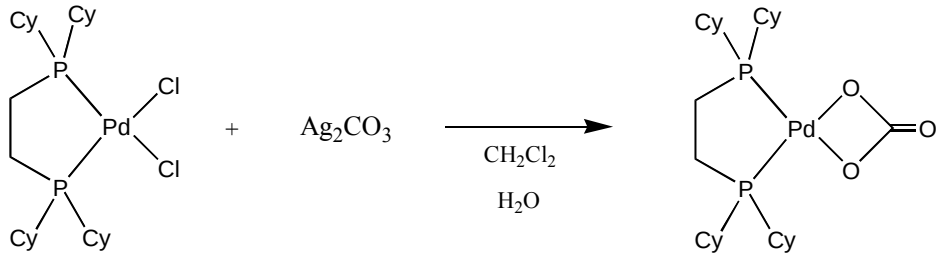
Scheme 7

Synthesis of Other Photochemical Precursors

Additional classes of photochemical precursors are also being synthesized using bis(dicyclohexylphosphino)ethane (dcpe) as the phosphine ligand. The complex (dcpe)Pd(pinacolate) has been synthesized by the reaction of pinacol ($HOCMe_2CMe_2OH$) with (dcpe)$PdCO_3$. Metal pinacolates often undergo photoextrusion of acetone leaving a reduced metal center. The photoreaction of (dcpe)Pd(pinacolate) would thus allow for an alternate means of generating the same low valent Pd intermediates as generated from the oxalate complexes. The advantage of pinacolate precursors is their greater solubility relative to the palladium oxalates in most organic solvents. Similarly, the photo-elimination of alkanes from dialkylpalladium complexes is being pursued. It has been found that (dcpe)$PdMe_2$ undergoes thermal and photochemical reductive elimination of ethane to generate (dcpe)Pd. The limited thermal stability of (dcpe)$PdMe_2$ has led us to synthesize the thermally more stable (dcpe)Pd$(CH_2SiMe_3)_2$ as a precursor complex.

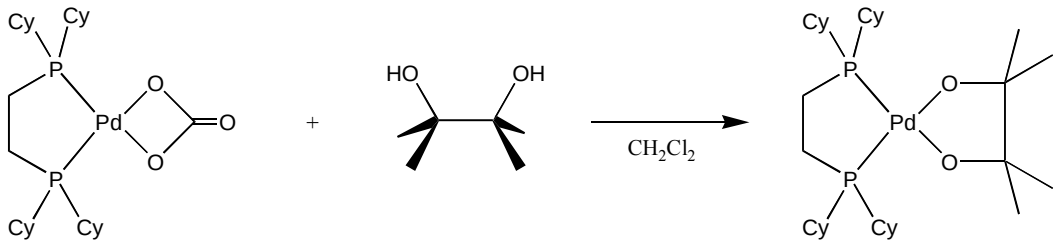
The complex (dcpe)$PdCl_2$ reacts with Ag_2CO_3 in wet CH_2Cl_2 in air to produce (dcpe)$PdCO_3$ (scheme 8). After filtering the AgCl from the reaction mixture, the solution gradually becomes dark yellow when left exposed to air. Transfer of the filtrate to a Schlenk flask and removing the solvent under vacuum slows the decomposition allowing for crystallization from CH_2Cl_2 with the addition of pentane. The $^{31}P\{^1H\}$ NMR

spectrum contains a single peak at 83.9 ppm. The $^{13}C\{^{1}H\}$ NMR spectrum contained two doublet of doublets at 35.4 and 21.5 ppm that would correspond to the methylene peaks in the phosphine backbone and the methine group of the cyclohexyl group. Additionally there is a doublet, a multiplet, and a singlet that are reasonable for the three other methylene groups of the cyclohexyl groups at 29.2, 27.1, and 26.2 ppm respectively. No discernable peak was observable for the carbonate under the experimental conditions the spectrum was obtained under. The IR of the crystals contains a strong stretching frequency at 1596 cm^{-1} with weaker shoulder peaks at 1619 and 1655 cm^{-1}.



Scheme 8

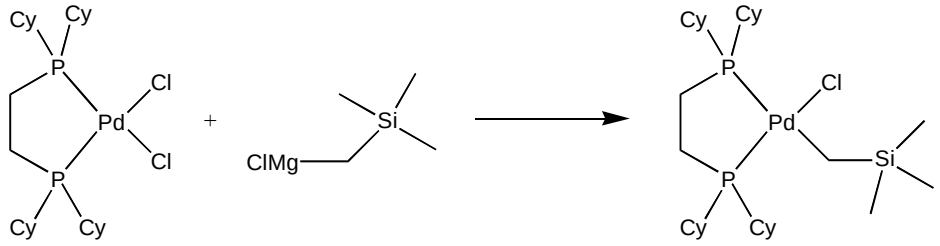
The complex (dcpe)$PdCO_3$ reacts with pinacol in CH_2Cl_2 with stirring at room temperature for two days to produce a new compound, possibly (dcpe)Pd(pinacolate) (Scheme 9). Crystals readily grow from CH_2Cl_2 and pentane at –20°. The $^{31}P\{^{1}H\}$ NMR spectrum obtained in C_6D_6 has a peak at 85.2 ppm. The ^{1}H NMR contains a broad peak at 2.8 ppm and multiplets between 2.2 and 1.2 ppm as well as a tall singlet at 1.20 ppm. Integration for all but the tall singlet compared to the tall singlet is about 26:12. Clear crystals grew on the inside of the NMR tube from the sample. The IR spectrum does not contain peaks seen for the carbonate complex and has a new peak at 1574 cm^{-1}.



Scheme 9

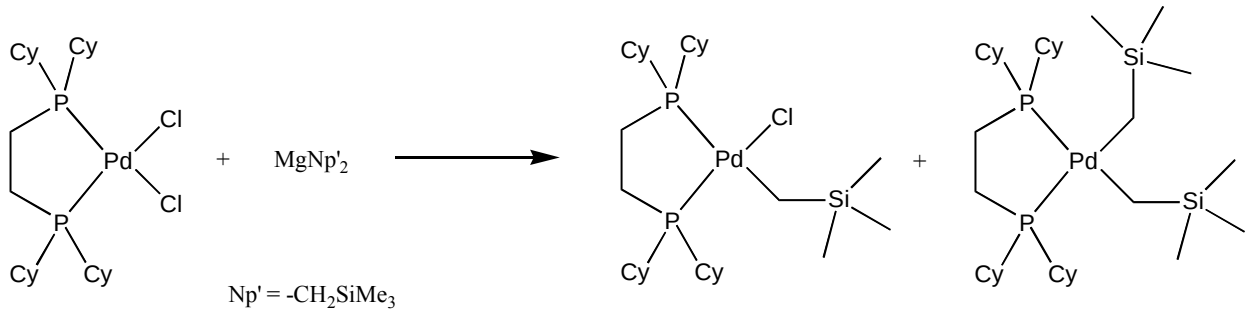
Treatment of (dcpe)$PdCl_2$ with an excess of (trimethylsilyl)methyl magnesium chloride in ethyl ether gives a mixture of starting material and (dcpe)$PdCl(CH_2SiMe_3)$ (Scheme 10). When the reaction is run in THF, the reaction mixture is homogeneous and generates more product. Ethyl ether extraction of the reaction mixture does preferentially dissolve the (dcpe)$PdCl(CH_2SiMe_3)$ over the (dcpe)$PdCl_2$ starting material but not selectively enough to separate them. An attempt to react a sample containing (dcpe)$PdCl_2$ and (dcpe)$PdCl(CH_2SiMe_3)$ with additional $Mg(CH_2SiMe_3)Cl$ in refluxing THF gave only (dcpe)$PdCl_2$ when observed by NMR spectroscopy in CD_2Cl_2.

The ^1H NMR of the (dcpe)$PdCl(CH_2SiMe_3)$ has multiplets between 1.2 and 2.2 ppm for the dcpe ligand. There is a doublet of doublets at 0.30 ppm for the two enantiotopic methylene protons of the (trimethylsilyl)methyl ligand and a singlet at 0.12 ppm for the methyl groups. Integration of the doublet of doublet to the singlet gives a ratio of 2 to 9 as expected. The $^{31}P\{^1H\}$ NMR spectrum has two doublets at 63.2 and 77.8 ppm as would be expected for two inequivalent phosphorus atoms in a phosphine metal complex.



Scheme 10

Treatment of dcpe$PdCl_2$ with an excess of $Mg(CH_2SiMe_3)_2$ generated *in situ* gave a mixture of (dcpe)$PdCl(CH_2SiMe_3)$ and (dcpe)$Pd(CH_2SiMe_3)_2$ (Scheme 10). Initial ethyl ether extraction gave only the two products. After a third extraction, only the (dcpe)$PdCl(CH_2SiMe_3)$ and a small amount of starting material was present. The ^1H NMR spectrum for (dcpe)$Pd(CH_2SiMe_3)$ contains a singlet at 0.03 ppm and a doublet of doublets at 0.25 ppm for the (trimethylsilyl)methyl group and multiplets 1.2 and 2.2 ppm for the dcpe ligand. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 55.5 ppm.



Scheme 10

Direct Observation of "(dcpe)Pd" by Nanosecond Flash Photolysis and Matrix Isolation Spectroscopy: Laser flash photolysis experiments have been performed on some of the palladium oxalates. In the case of (dcpe)Pd(oxalate), laser photolysis in acetonitrile results in a transient with an optical absorption near λ_{max} = 330 nm. The transient has been tentatively identified as the low coordinate bisphosphine palladium species, (dcpe)Pd. This transient species is relatively long lived on the microsecond time scale. Figure 2 shows a spectrum obtained from a series of absorption vs. time measurements taken at wavelengths between 285 and 400 nm over a period of 90μs. Assignment of the transient at 330nm as "(dcpe)Pd" is supported by the independent photolysis of (dcpe)Pd(oxalate) in a butyronitrile glass at 77 K (Figure 3).

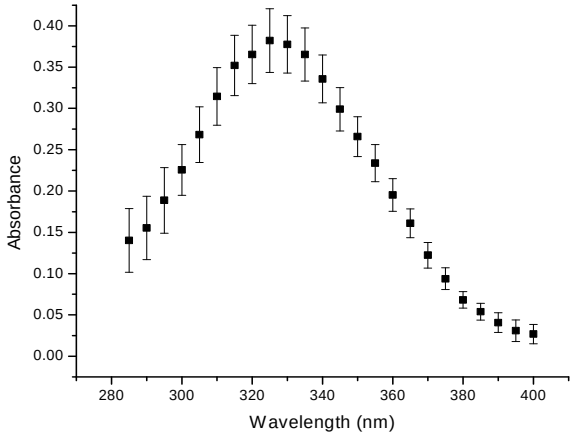


Figure 2. Transient spectrum generated from the 266nm laser flash photolysis of (dcpe)Pd(oxalate) in CH_3CN

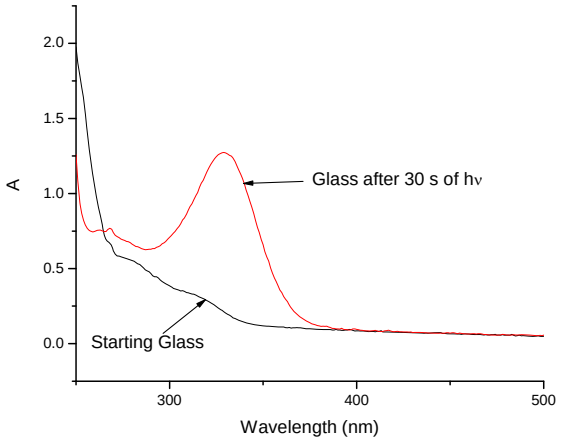


Figure 3. 254nm photolysis of (dcpe)Pd(oxalate) in *n*-PrCN at 77K.

Photolysis of other Bis(phosphine) Oxalates

The photochemistry of the other bis(phpsphine) oxalates was also examined in butyronitrile glass. The 254nm photolysis of these precursors gave new transients with UV absorptions close to that found for (dcpe)Pd (~ 330nm). Figure xxx shows the UV spectra from the formation of these matrix stabilized intermediates in nPrCN at 77K. The band positions of the long wavelength absorptions are largely insensitive to chelate ring size but show a slight hypsochromic shift with increasing ring size. Other features between 250-300 nm are also present. The matrix spectra disappear upon annealing consistent with assignments of the bands to (P^P)Pd species. Table 2 summarizes the optical properties of the (P^P)Pd as a function of ligand.

ligand	(nm)	(nm)
dcpm	-	329
dcpe	267	330
dcpp	278	325
dcpb	284	319

Table 2 Absorption Maxima of (P^P)Pd in ^{n}PrCN glass at 77K

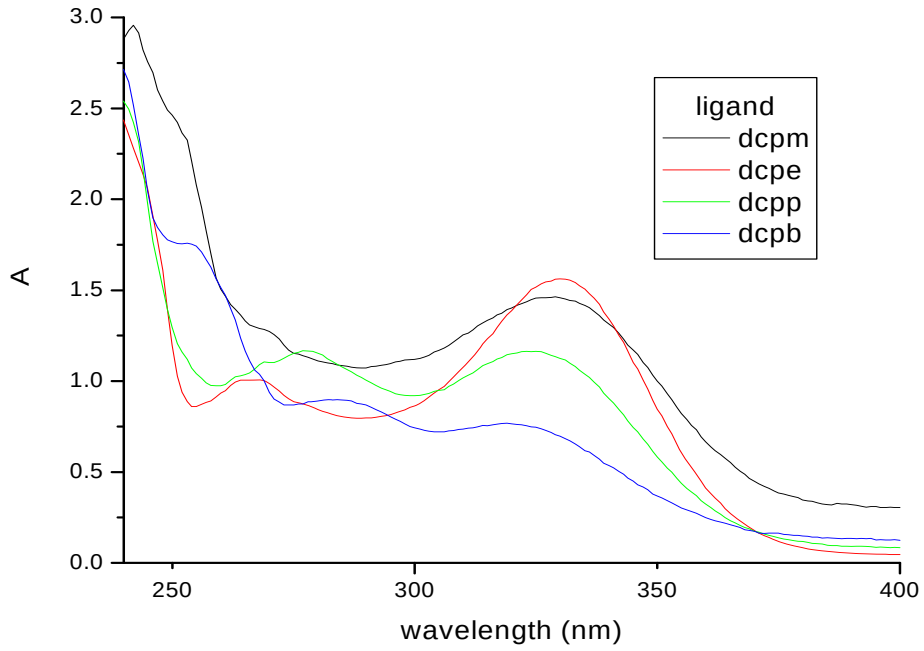


Figure 4 Absorption Spectra of (P^P)Pd in ^{n}PrCN glass at 77K

Kinetic Studies of Reactions of (dcpe)Pd with Silanes: The reaction of silanes with low valent metals can potentially serve as models for catalytic C-H activation in hydrocarbons. Previously, we have found from NMR studies that Si-H σ-complexes may be important intermediates for the activation of silanes by palladium. We are currently looking for further mechanistic evidence for these complexes by examining the reaction kinetics between photogenerated "(dcpe)Pd" with silanes. One experiment that is being performed with Etsuko Fujita at BNL is the flash photolysis of (dcpe)Pd(H)($SiPh_3$). Photochemically, the silane may undergo reductive elimination to give free "(dcpe)Pd" and silane. The fast kinetics of thermal recombination may then be followed. This type of experiment is an example of "off-on" chemistry. Dr. Fujita (BNL) has much experience with this type of chemistry in regard to C-H σ-complexes. Initially, we were hopeful to follow the reaction by fast IR techniques; however, the intensity of the ν(Pd-H) and ν(Si-H) stretching vibrations were found to be too weak (~ 55 M^{-1} cm^{-1}).

Experimental Section

(tmeda)PdC_2O_4: The complex (tmeda)$PdCl_2$ (1.207 g, 3.974 mmol) was combined with $Ag_2C_2O_4$ (0.972 g, 3.31 mmol) and 50 mL of CH_2Cl_2. The mixture was refluxed for 12 h giving a yellow solution with yellow suspension. After filtration through filter paper in air, the filter paper was tightly folded and placed in a 125 mL soxhlet extractor and extracted with 100 mL of distilled dry CH_2Cl_2 for two days resulting in a yellow solution with yellow suspended solid. Filtration of the mixture a frit gave light yellow solid (tmeda)PdC_2O_4 (0.556 g, 1.79 mmol) and a clear yellow filtrate. The addition of pentane and storage at –20°C gave yellow crystals of (tmeda)PdC_2O_4 (0.177 g, 0.570 mmol, combined yield 71%). ^{1}H NMR (CD_3SOCD_3): δ 2.65 (s, 12 H, NC*H*$_3$), 2.79 (s, 4 H, -C*H*$_2$-). $^{13}C\{^1H\}$ NMR (CD_3SOCD_3): δ 49.72 (s, N*C*H_3), 60.95 (s. –*C*H_2), 165.66 (s, -O*C*(O)*C*(O)O-). IR (KBr): ν_{CO} 1703, 1678, and 1660 cm^{-1}. Anal. Calcd for $C_8H_{16}N_2O_4Pd$: C, 30.93; H, 5.19; N, 9.02. Found C, 31.06; H, 5.20; N, 8.90.

(dcpm)PdC_2O_4: The complex (tmeda)PdC_2O_4 (0.098 g, 0.315 mmol) was suspended in 8 mL of CH_2Cl_2 and dcpm (0.182 g, 0.445 mmol) dissolved in 16 mL of CH_2Cl_2 was added. After stirring for 12 h, 20 mL of pentane was added to the mixture with white

suspended solid and the mixture was cooled to –20° C. The white solid was collected by filtration and dried under vacuum to give (dcpm)PdC_2O_4 (0.183 g, 0.303 mmol, 96%). After washing the white solid with CH_2Cl_2, the material was analyzed for (dcpm)$PdC_2O_4 \cdot H_2O$. ^{1}H NMR (CD_2Cl_2): δ 1.2-2.2 (m, 44 H, Cy), 2.83 (t, J_{PH} = 10 Hz, 2 H, PCH_2P). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –26.68. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 18.8 (t, J_{PC} = 24 Hz, P*C*H$_2$P), 26.0 (s, Cy), 27.1 (t, J_{PC} = 6 Hz Cy), 27.2 (t, J_{PC} = 7 Hz Cy), 29.3 (s, J_{PC} = 22 Hz, Cy), 29.6 (s, Cy), 35.2 (t, J_{PC} = 10 Hz, -*C*HP-). IR (KBr): ν_{CO} 1656 (s), 1702 (w), 1637 (sh). Anal. Calcd for $C_{27}H_{48}O_5P_2Pd$: C, 52.22; H, 7.79. Found C, 52.43; H, 7.71.

(dcpp)PdC_2O_4: The complex (tmeda)PdC_2O_4 (0.110 g, 0.354 mmol) was suspended in 8 mL of CH_2Cl_2 and dcpp (0.217 g, 0.497 mmol) dissolved in 16 mL of CH_2Cl_2 was added. After stirring for 1 h, 15 mL of pentane was added to the clear colorless solution and the mixture was cooled to –20° C. And additional 15 mL of pentane was added 1 d later. White solid formed and was collected by filtration and dried under vacuum to give (dcpp)PdC_2O_4 (0.124 g, 0.196 mmol, 55%). The addition of pentane to the filtrate and additional cooling to –20°C gave a second crop of (dcpp)PdC_2O_4 (0.054 g, 0.086 mmol, 24%). ^{1}H NMR (CD_2Cl_2): δ 1.2-2.3 (m, 50 H, Cy, -CH_2-). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 31.5. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 15.73 (dd, J_{PC} = 18, 17 Hz, P*C*H$_2$-), 22.76 (s, PCH$_2$*C*H$_2$-), 26.37 (s, Cy), 27.18 (t, J_{PC} = 5 Hz, Cy), 27.46 (t, J_{PC} = 7 Hz, Cy), 29.20 (s, Cy), 30.18 (s, Cy), 35.29 (m -*C*HP-), 167.33 (t, J_{PC} = 1 Hz, -O*C*(O)*C*(O)O-). IR (KBr): ν_{CO} 1668 (s), 1697 (m), 1646 (m). Anal. Calcd for $C_{29}H_{50}O_4P_2Pd$: C, 55.19; H, 7.99. Found C, 55.00; H, 8.05.

(dcpb)PdC_2O_4: The complex (tmeda)PdC_2O_4 (0.90 g, 0.290 mmol) was suspended in 15 mL of CH_2Cl_2 and dcpb (0.138 g, 0.306 mmol) dissolved in 15 mL of CH_2Cl_2 was added. After stirring for 12 h, yellow solid was filtered from the mixture to give a clear colorless solution. The addition of 15 mL of pentane and cooling to –20°C gave (dcpb)PdC_2O_4 as a white solid that was collected by filtration and dried under vacuum (0.091 g, 0.141 mmol, 49%). ^{1}H NMR (CD_2Cl_2): δ 1.2-2.3 (m, 50 H, Cy, -CH_2-). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 46.85. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 16.6 (dd, J_{PC} = 15, 13 Hz, P*C*H$_2$-), 23.4 (s, PCH$_2$*C*H$_2$-), 26.5 (s, Cy), 27.3 (t, J_{PC} = 5 Hz, Cy), 27.8 (t, J_{PC} = 5 Hz, Cy), 29.2 (s, Cy), 30.8 (s, Cy), 35.6 (m, -*C*HP-), 167.31 (t, J_{PC} = 1 Hz, -O*C*(O)*C*(O)O-). IR (KBr):

ν_{CO} 1673 (s), 1697 (m), 1647 (m). Anal. Calcd for $C_{29}H_{52}O_4P_2Pd{\cdot}CH_2Cl_2$: C, 51.00; H, 7.46. Found C, 51.22; H, 7.73.

(dcpe)PdCl$_2$: The complex $(MeCN)_2PdCl_2$ (0.589 g, 2.27 mmol) was suspended in 30 mL of THF and a 15 mL THF solution containing dcpe (0.965 g, 2.28 mmol) was added. After stirring for 12 h there is a white solid suspension of (dcpe)$PdCl_2$. The product was collected by filtration and dried under vacuum (1.299 g, 2.17 mmol, 95%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 94.6.

(dcpe)PdC$_2$O$_4$: A mixture of (dcpe)$PdCl_2$ (0.297 g, 0.495 mmol) and $Ag_2C_2O_4$ (0.808 g, 2.65 mmol) were refluxed in MeOH for 12 h resulting in a black suspension. The mixture was filtered and the collected solid was extracted with CH_2Cl_2. The solvent was removed and the residue was recrystallized from CH_2Cl_2 and pentane to get (dcpe)PdC_2O_4 (0.231 g, 0.374 mmol, 76%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 89.8. UV-vis (MeCN): λ_{max} (log ε) 212 (4.50) nm. IR (KBr): ν_{CO} 1662 (s), 1698 (m), 1639 (m).

(dcpe)Pd(CH$_2$SiMe$_3$)$_2$: An excess of $MgBr(CH_2SiMe_3)$ (1.0 M ether, mL, mmol) was added to a rapidly stirred suspension of (dcpe)$PdCl_2$ (g, mmol) in 15 mL of THF resulting in a clear solution within 1 min. After stirring 2h, the reaction was quenched with aqueous NH_4Cl, the THF and water layers separated, and the solvent was removed. The white residue was extracted with a minimum of THF and the volume was tripled with layered pentane. Crystals formed at –20°C and were collected on a frit, washed with pentane, and dried under vacuum to yield light yellow plates (0.104 g, 0.148 mmol, 44% yield). Crystals submitted for analysis were grown from CH_2Cl_2 and Et_2O. ^1H NMR (CD_2Cl_2): δ 0.03 (s, 18 H, Si*Me$_3$*), 0.25 ($AB_{quartet}$)(t, 4H, J_{AB} = 4 Hz), 1.1-1.4 (m, 20 H, *Cy*), 1.5-2.1 (m, 28 H, *Cy*, C*H$_2$*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 57.7 $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ –2.03 (dd, J_{PC} = 96, 9 Hz, Pd*C*H_2Si), 5.62 (s, *C*H_3), 22.81 (t, J_{PC} = 19 Hz, P*C*H_2*C*H_2P), 26.79 (s, *Cy*), 27.8 (m, *Cy*), 29.70 (t, J_{PC} = 2 Hz, *Cy*), 35.0 (m, -*C*HP-). $^{29}Si\{^1H\}$ NMR (CD_2Cl_2): δ 0.73 (d, J_{PSi} = 3 Hz). Anal. Calcd for $C_{34}H_{70}P_2PdSi_2$: C, 58.05; H, 10.03. Found C, 57.87; H, 10.37.

(dcpe)Pd(CH$_2$SiMe$_3$)Cl: An excess of $MgBr(CH_2SiMe_3)$ (1.0 M ether, 0.8 mL, 0.8 mmol) was added to a rapidly stirred suspension of (dcpe)$PdCl_2$ (0.237 g, 0.395 mmol) in 15 mL of THF resulting in a clear solution within 1 min. After stirring for 4 min, the

reaction was quenched with aqueous NH_4Cl, the THF and water layers separated, and the solvent mostly removed. The white pasty mixture was extracted with 90 mL of acetone, the solution filtered, and the solvent removed to get a white solid (0.184 g, 66% yield). Recrystallization from CH_2Cl_2 and Et_2O gave needle crystals. ^{1}H NMR (CD_2Cl_2): δ 0.12 (s, 9 H, Si*Me*$_3$), 0.28 ($AB_{quartet}$)(d, 1H, J_{AB} = 4 hz), 0.32 ($AB_{quartet}$)(d, 1H, J_{AB} = 4 hz), 1.13-2.19 (m, 48 H, *dcpe*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 63.87 (d, J_{pp} = 16 Hz), 78.40 (d, J_{pp} = 16 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 5.09 (d, J_{PC} = 3 Hz, *C*H$_3$), 7.55 (dd, J_{PC} = 94, 3 Hz, Pd*C*H$_2$Si), 19.28 (d, J_{PC} = 10 Hz, P*C*H$_2$), 19.52 (d, J_{PC} = 10 Hz, P*C*H$_2$), 26.56 (s, *Cy*), 26.73 (s, *Cy*), 27.39 (s, *Cy*), 27.52 (s, *Cy*), 27.60 (d, J_{PC} = 3 Hz, *Cy*), 27.72 (d, J_{PC} = 4 Hz, *Cy*), 29.14 (s, *Cy*), 29.29 (d, J_{PC} = 2 Hz, *Cy*), 29.64 (d, J_{PC} = 4 Hz, *Cy*), 30.00 (d, J_{PC} = 2 Hz, *Cy*), 34.63 (d, J_{PC} = 15 Hz, -*C*HP-), 36.36 (d, J_{PC} = 27 Hz, -*C*HP-). ^{29}Si{^{1}H} NMR (C_6H_6): δ 1.7 (dd, J_{PSi} = 5, 2 Hz). Anal. Calcd for $C_{30}H_{59}ClP_2PdSi$: C, 55.29; H, 9.32. Found C, 51.65; H, 8.62.

(dcpe)Pd(CH$_2$SiMe$_3$)Me: An excess of MeLi (1.6 M in ether, 0.5 mL, 0.8 mmol) was added to a rapidly stirred suspension of (dcpe)Pd(CH_2SiMe_3)Cl (0.064 g, 0.098 mmol) in 15 mL of Et_2O. The mixture became clear after 1 min and was stirred for 1 hr before quenching with DI H_2O. Isolated Et_2O mixture and removed solvent *in vacuo*. The white residue was dissolved in 3 mL of THF, filtered through celite and concentrated to almost dryness before layering with 1 mL of Et_2O. Crystals formed at –20^{o}C overnight. The solvent was decanted, the crystals rinsed with Et_2O and dried *in vacuo* to give light yellow crystals (0.025 g, 0.040 mmol, 41% yield).

^{1}H NMR (C_6D_6): δ 0.60 (s, 9 H, Si*Me*$_3$), 0.75, 0.76 ($AB_{quartet}$, 2 H, J_{AB} = 9 Hz, -C*H*$_2$SiMe$_3$), 0.87 (t, 3 H, J_{HP} = 7 Hz, Pd*Me*), 1.0-1.46 (m, 24 H, *Cy*PdC*H*$_2$-), 1.46-1.80 (m, 16 H, *Cy*), 1.90 (m, 4 H, *Cy*), 2.08 (t, 4 H, *J* = 15 Hz, *Cy*).). ^{31}P{^{1}H} NMR (C_6D_6): δ 57.60 (d, J_{PP} = 9 Hz), 59.07(d, J_{PP} = 9 Hz). ^{13}C{^{1}H} NMR (C_6H_6): δ –0.90 (dd, J_{PC} = 109, 10 Hz, Pd*C*H$_3$), 0.94 (dd, J_{PC} = 94, 8 Hz, Pd*C*H$_2$Si), 6.51 (d, J_{PC} = 3 Hz, Si*Me*$_3$), 23.17 (dd, J_{PC} = 17, 4 Hz, P*C*H$_2$), 23.45 (dd, J_{PC} = 17, 4 Hz, P*C*H$_2$), 26.90 (d, J_{PC} = 1 Hz, *Cy*), 26.97 (d, J_{PC} = 1 Hz, *Cy*), 27.66 (d, J_{PC} = 3 Hz, *Cy*), 27.8 (overlapping d, J_{PC} = 3 Hz, *Cy*), 27.79 (s, *Cy*), 27.95 (d, J_{PC} < 1 Hz, *Cy*), 29.14 (s, *Cy*), 29.21 (s, *Cy*), 29.84 (d, J_{PC} = 5 Hz, *Cy*), 29.95 (d, J_{PC} = 5 Hz, *Cy*), 35.03 (d, J_{PC} = 16 Hz, -*C*HP-), 35.18 (d, J_{PC} =

14 Hz, -*C*HP-). $^{29}Si\{^1H\}$ NMR (CD_2Cl_2): δ 1.05 (d, J_{PSi} = 5 Hz). Anal. Calcd for $C_{31}H_{62}P_2PdSi$: C, 58.98; H, 9.90. Found C, 58.76; H, 10.22.

(dtbpe)$PdCl_2$:

^1H NMR (CD_2Cl_2): δ 1.51 (d, J_{PH} = 14 Hz, 36 H, CH_3), 2.01 (d, J_{PH} = 14 Hz, 4 H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 25.29 (dd, J_{PC} = 17, 16 Hz, *C*H_2), 30.83 (s, *C*H_3), 39.32 (dd, J_{PC} = 10, 9 Hz, *C*Me_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 106.96.

(dtbpe)PdC_2O_4:

^1H NMR (CD_2Cl_2): δ 1.48 (d, J_{PC} = 14 Hz, 36 H, CH_3), 2.06 (d, J_{PC} = 12 Hz, 4 H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ Anal. Calcd for $C_{20}H_{40}O_4P_2Pd{\cdot}H_2O$: C, 45.25; H, 7.97. Found C, 45.49; H, 8.07.

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Number of Undergraduates Supported by DOE

Lisa Linehardt: Lisa Linehardt was an undergraduate at Tulane. She works part time in my laboratory as a work-study student assisting on the project. She was a chemistry major and did a Honor's thesis based on work associated with the project. She is currently a graduate student in Chemistry at Georgia Tech.

Number of Graduate Students Supported by DOE

Daniel Sattler: Daniel Sattler is a graduate student with a 4 year fellowship from the Louisiana Board of Regents. He will be pursuing his doctoral work entirely based on the project.

Number of Postdoctoral Fellows Supported by DOE

Douglas Pool: Douglas Pool is a recent graduate from the University of Illinois (Pat Shapley's group). He was entirely supported by the DOE grant and will be the go-between for here and Brookhaven National Laboratories.

Publications Related to DoE Project

Boyle, Robert C.; Mague, J.T., Fink, M.J. "*X-Ray Crystal Structure of N,N,N'N'-Tetramethylethylenediamine Palladium(II) Chloride*", Acta Cryst. E, **2004**, *E60*, m40-m41

Boyle, Robert C.; Mague, J.T.; Fink, M.J. *"(μ-1,2-Bis(dicyclohexylphosphino)ethane)-κ^2P:P'- bis{[1,2-bis(di-cyclohexylphosphino)ethane)-κ^2P:P']-palladium(0)}*", Acta Cryst. E , **2004**, *E60*, m625-m627

Jacobsen, H.; Fink, M.J. "*Tuning the Palladium-Silicon Bond: Bonding in Bisphosphine Palladium Silicon Hydrides*" Organometallics**, 2006**, *25*, 1945-1952

Boyle, R.C.; Fink, M.J. *"Evidence for Long Lived Si-H and Si-Si Sigma Complexes with Palladium",* J. Am. Chem. Soc., **2006**, 128, 9054

Mague, J.T.; Pool, D.H., Fink, M.J. "*cis-Dichlorido[bis(dicyclohexylphosphine)methane-κ^2 P,P'} palladium(II) dichloromethane solvate*" Acta Cryst. , **2007**, *E63*, m3083

Presentations Related to DoE Project

Mark J. Fink, Joel T. Mague, and Robert C. Boyle "Activation of Si-H and Si-Si Bonds by Palladium Bisphosphine Complexes: Evidence for Long Lived σ-Complexes", 37th Silicon Symposium, Philadelphia, PA, May 20-22, 2004

Mark J. Fink "Sigma Complexes of Si-H and Si-Si Bonds to Palladium: Their Involvement in Some Extraordinary Kinetic Isotope Effects" NSF Inorganic Workshop, Sodona, AZ, June 8-11, 2004

Doug Pool and Mark J. Fink "Sigma Bond Activation by Low Valent Palladium Complexes: NMR and Nanosecond Laser Flash Photolysis Studies" NSF/DOE EPSCoR Conference, Argonne, IL, June 14-16

Mark J. Fink, Joel T. Mague and Robert C. Boyle, "Activation Of Si-H Bonds And Si-Si Bonds By Palladium Bisphosphine Complexes: Evidence For Long Lived Sigma Complexes", 36th International Conference on Coordination Chemistry, Merida, Mexico, July 18, 2004

Doug H. Pool, Robert C. Boyle, and Mark J. Fink, "Investigation of Low Valent Palladium" 5th Louisiana Conference on Advanced Materials and Emerging Technologies, New Orleans, January 21-22, 2005

Mark J. Fink, "Low Valent Palladium Complexes and Their Interactions with Silanes", MacMaster University, Hamilton, Ontario, CANADA, April 13, 2006

Mark J. Fink "Low Valent Palladium Complexes and Their Interactions with Silanes", University of Missouri, St. Louis, St. Louis, MO, April 24, 2006

Mark J. Fink, "Low Valent Palladium Complexes and Their Interactions with Silanes", Washington University, St. Louis, MO, April 25, 2006

Doug H. Pool, Robert C. Boyle, and Mark J. Fink, "*Investigation of Low Valent Palladium*" 5th Louisiana Conference on Advanced Materials and Emerging Technologies, New Orleans, January 21-22, 2005

Mark J. Fink, Joel T. Mague, Doug Pool, and Robert C. Boyle "*Activation of Si-H and Si-Si Bonds by Palladium Bisphosphine Complexes: The Role of Long Lived σ-Complexes*" 14th International Symposium on Organosilicon Chemistry, Wurzberg, GERMANY, July 31-August 5, 2005

Mark J. Fink, Joel T. Mague, Doug Pool, Heiko Jacobsen, and Robert C. Boyle, "*Dynamic Behavior in Silyl Palladium Hydrides and Related Complexes: Evidence for Long Lived Si-H and Si-Si Sigma Complexes*" PACIFICHEM, Honolulu, HI, December 19, 2005